

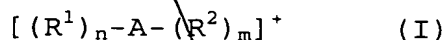
CLAIMS

- sub A, >
1. A process for carrying out impregnation and/or for preparing a coating which gives release and is leaktight employed at the engine block/cylinder head interface of engines and applied in particular to sheet gaskets, in particular cylinder head gaskets, characterized in that it consists essentially:
- 1 - in employing a silicone composition comprising:
- A- 100 parts by weight of at least one polyorganosiloxane (POS) crosslinkable by the cationic and/or radical route and via crosslinking functional groups (CFGs), these CFGs being identical to or different from one another and being chosen from those comprising at least one functional unit of heterocyclic nature having one or more electron-donating atoms and/or from those which are ethylenically unsaturated and substituted by at least one electron-donating atom which enhances the basicity of the π system;
- B- from 0.01 to 10 parts by weight of at
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least one initiator salt (PI) formed by a borate of an onium of an element from groups 15 to 17 of the Periodic Classification [Chem. & Eng. News, Vol. 63, No. 5, 26 of February 4, 1985] or of an organometallic complex of an element from groups 4 to 10 of the Periodic Classification (same reference),

□ the cationic entity of said borate being chosen from:

(1) - onium salts of formula (I):



in which formula:

- A represents an element from groups 15 to 17;
- R^1 represents a C_6 - C_{20} carbocyclic or heterocyclic aryl radical, it being possible for said heterocyclic radical to comprise nitrogen or sulfur as heteroelements;
- R^2 represents R^1 or a linear or branched C_1 - C_{30} alkyl or alkenyl radical; said R^1 and R^2 radicals

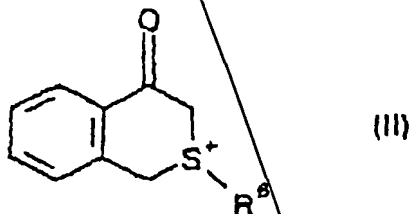
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optionally being substituted by a C₁-C₂₅ alkoxy, C₁-C₂₅ alkyl, nitro, chloro, bromo, cyano, carboxy, ester or mercapto group,

- n is an integer ranging from 1 to v + 1, v being the valency of the element A,
- m is an integer ranging from 0 to v - 1, with n + m = v + 1,

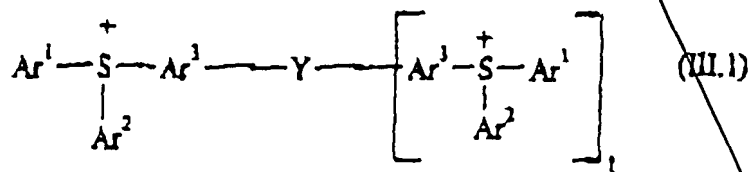
(2) - the oxoisoithiochromanium salts having the formula:



where the R⁶ radical represents a linear or branched C₁-C₂₀ alkyl radical;

(3) - sulfonium salts where the cationic entity comprises:

→ 3.1. at least one polysulfonium species of formula III.1



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in which:

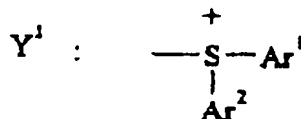
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- the Ar^1 symbols, which can be identical to or different from one another, each represent a monovalent phenyl or naphthyl radical optionally substituted with one or more radicals chosen from: a linear or branched $\text{C}_1\text{-C}_{12}$ alkyl radical, a linear or branched $\text{C}_1\text{-C}_{12}$ alkoxy radical, a halogen atom, an -OH group, a -COOH group, a -COO-alkyl ester group, where the alkyl part is a linear or branched $\text{C}_1\text{-C}_{12}$ residue, and a group of formula $-\text{Y}^4\text{-Ar}^2$, where the Y^4 and Ar^2 symbols have the meanings given immediately below,
 - the Ar^2 symbols, which can be identical to or different from one another or Ar^1 , each represent a monovalent phenyl or naphthyl radical optionally substituted with one or more radicals chosen from: a linear or branched $\text{C}_1\text{-C}_{12}$ alkyl radical, a linear or branched $\text{C}_1\text{-C}_{12}$ alkoxy radical, a halogen atom, an -OH group, a -COOH group or a -COO-alkyl ester group, where the alkyl part is a linear or branched $\text{C}_1\text{-C}_{12}$ residue,
 - the Ar^3 symbols, which can be identical to or different from one another, each represent a divalent phenylene or naphthylene radical optionally substituted with one or more radicals

chosen from: a linear or branched C₁-C₁₂ alkyl radical, a linear or branched C₁-C₁₂ alkoxy radical, a halogen atom, an -OH group, a -COOH group or a -COO-alkyl ester group, where the alkyl part is a linear or branched C₁-C₁₂ residue,

- t is an integer equal to 0 or 1,

with the additional conditions according to which:

+ when t = 0, the Y symbol is then a Y¹ monovalent radical representing the group of formula:

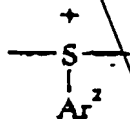


where the Ar¹ and Ar² symbols have the meanings given above,

+ when t = 1:

* on the one hand, the Y symbol is then a divalent radical having the following meanings Y² to Y⁴:

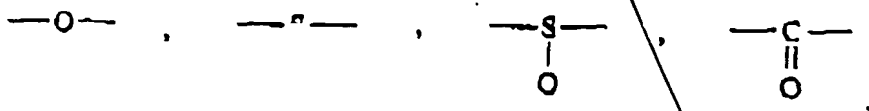
• Y²: a group of formula:



where the Ar² symbol has the meanings given above,

• Y³: a single valency bond,

• Y⁴: a divalent residue chosen from:



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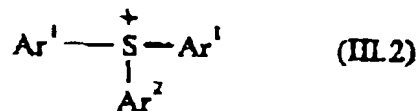
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a linear or branched C₁-C₁₂ alkylene
residue and a residue of formula
-Si(CH₃)₂O-,

* on the other hand, solely in the case
where the Y symbol represents Y³ or Y⁴,
the Ar¹ and Ar² (terminal) radicals have,
in addition to the meanings given above,
the possibility of being connected to
one another via the Y' residue
consisting in Y'¹, a single valency bond,
or in Y'², a divalent residue chosen from
the residues cited with respect to the
definition of Y⁴, which is inserted
between the carbon atoms, facing each
other, situated on each aromatic ring in
the ortho position with respect to the
carbon atom directly bonded to the S⁺
cation;

→ 3.2. and/or at least one monosulfonium
species having a single S⁺ cationic
center per mole of cation and
consisting, in the majority of cases, in
species of formula:



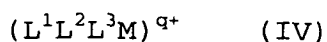
in which Ar¹ and Ar² have the meanings given above with

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respect to the formula (III.1), including the possibility of connecting directly between them only one of the Ar^1 radicals to Ar^2 according to the way indicated above with respect to the definition of the additional condition in force when $t=1$ in the formula (II) involving the Y' residue;

(4) organometallic salts of formula (IV):



in which formula:

- M represents a metal from group 4 to 10,
- L^1 represents 1 ligand bonded to the metal M via π electrons, which ligand is chosen from η^3 -alkyl, η^5 -cyclopentadienyl and η^7 -cycloheptatrienyl ligands and η^6 -aromatic compounds chosen from optionally substituted η^6 -benzene ligands and compounds having from 2 to 4 condensed rings, each ring being capable of contributing to the valency layer of the metal M via 3 to 8 π electrons,
- L^2 represents a ligand bonded to the metal M via π electrons, which ligand is chosen from η^7 -cycloheptatrienyl ligands and η^6 -aromatic compounds chosen from optionally substituted η^6 -benzene ligands and compounds having from 2 to 4 condensed rings, each ring being capable of contributing to the valency layer of the

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metal M via 6 or 7 π electrons,

• L^3 represents from 0 to 3 identical or different ligands bonded to the metal M via σ electrons, which ligand(s) is (are) chosen from CO and NO_2^+ ; the total electronic charge q of the complex to which L^1 , L^2 and L^3 and the ionic charge of the metal M contribute being positive and equal to 1 or 2;

□ the anionic entity [lacuna] borate having the formula:



in which formula:

- a and b are integers ranging from 0 to 3 for a and from 1 to 4 for b, with

$$a + b = 4,$$

- the X symbols represent:

* a halogen atom with $a = 0$ to 3,

* an OH functional group with $a = 0$ to 2,

- the R symbols are identical or different and represent:

▷ a phenyl radical substituted by at least one electron-withdrawing group and/or by at least 2 halogen atoms, this being when the cationic entity is an onium of an element from groups 15 to 17,

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- 5 ▷ a phenyl radical substituted by at least
 one electron-withdrawing element or
 group, this being when the cationic
 entity is an organometallic complex of
 an element from groups 4 to 10,
- 10 ▷ an aryl radical comprising at least two
 aromatic nuclei, which is optionally
 substituted by at least one electron-
 withdrawing element or group, whatever
 the cationic entity;
- 15 -C- 1 to 50 parts by weight of at least one
 reactive diluent consisting in a
 nonorganosilicon organosilicon or
 organic compound comprising, in its
 structure, at least one CFG as defined
 above and optionally at least one
 secondary functional group (SFG) other
 than a CFG but capable of reacting
 chemically with a CFG;
- 20 -D- 0 to 10 parts by weight of at least one
 pigment;
- E- 0 to 100 parts by weight of a filler of
 inorganic nature;
- 25 -F- 0 to 10 parts by weight of at least one
 photosensitizer;
- G- 0 to 10^{-2} part by weight of a stabilizer

consisting in at least one stabilizing
amine agent,

-H- 0 to 5 parts by weight of an adhesion
promoter;

5 2 - in applying this composition to a
support (cylinder head sheet gasket or cylinder head/
engine block interface), and

3 - in crosslinking the applied composition
by photochemical and/or thermal activation and/or under
10 an electron beam.

2. The process as claimed in claim 1,
characterized in that the support is a metal cylinder
head gasket.

3. The process as claimed in claim 2,
15 characterized in that the support is a metal multilayer
cylinder head gasket and in that a coating is formed on
at least one of the faces of at least one of the layers
composing the metal multilayer cylinder head gasket.

4. The process as claimed in any one of
20 claims 1 to 3, characterized in that the functional
units included in the CFG groups are selected from the
group of following units:

- an ethylenically unsaturated and activated
functional group,

25 - epoxide,
 - oxethane,

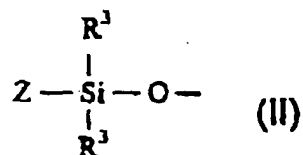
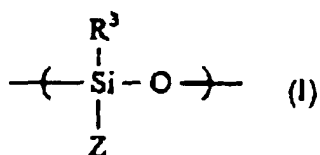
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- and their mixtures,
and in that the functional units included in the
optional SFG groups are selected from the group of
following units:

- 5 - hydroxyl,
 - alkoxy,
 - carboxyl,
 - and their mixtures.

5. The process as claimed in any one of
10 claims 1 to 4, characterized in that the POSSs A are
 epoxysilicones and/or vinyl ether silicones which are:
 → either linear or substantially linear and composed of
 units of formula (I), terminated by units of formula
 (II),
15 → or cyclic and composed of units of formula (II):



in which formulae:

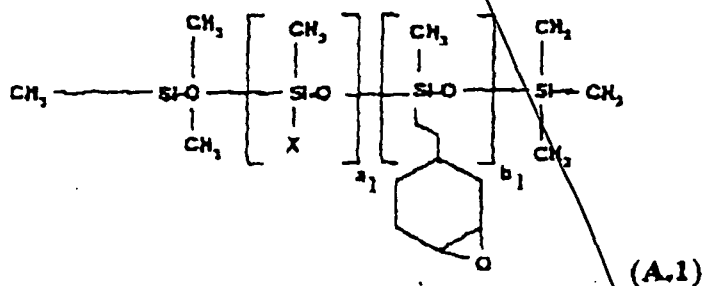
- 20 • the R^3 symbols are alike or different and represent:
- either a hydroxyl radical,
 - or a linear or branched $\text{C}_1\text{-C}_{18}$ alkyl radical
 which is optionally substituted by one or
 more halogens and/or a hydroxyl radical,

25 - or a $\text{C}_2\text{-C}_8$ alkenyl radical,

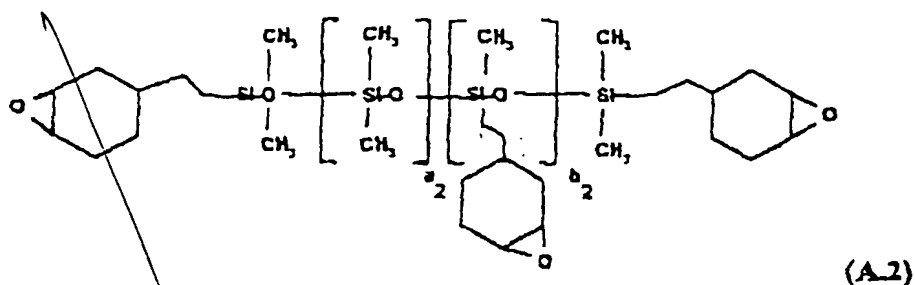
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- or an optionally substituted C₅-C₈ cycloalkyl radical,
 - or an aryl or aralkyl radical which is optionally substituted by halogens and/or alkoxy,
 - 5 • the Z symbols are alike or different and represent:
 - either the R³ radical,
 - or a CFG group corresponding to an epoxide or vinyl ether residue connected to the silicon via a divalent radical comprising from 2 to 20 carbon atoms and optionally comprising a heteroatom,
 - 10 at least one of the Z symbols corresponding to a CFG group.

15 6. The process as claimed in any one of claims 1 to 5, characterized in that the POSS A are epoxysilicones of formula (A.1), (A.2) and (A.3):



20 with X = CH₃; phenyl; C₅-C₈ cycloalkyl; C₁-C₁₈ alkyl; C₂-C₈ alkenyl; -OH; H; -CH₂-CH₂-CH₂-OH; -CH₂-CH₂-CF₃ or -(CH₂)_n-CF₃, n = 1 to 20;



- a_1 , a_2 , b_1 and b_2 being defined as follows in these formulae (A.1) and (A.2)

$$1 \leq a_1, a_2$$

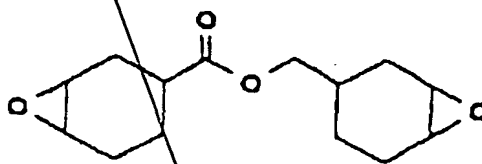
$$1 \leq b_1, b_2$$

- 5 - a_2 and b_2 being = 0 in the formula (A.2) to give the epoxidized disiloxane (A.3).

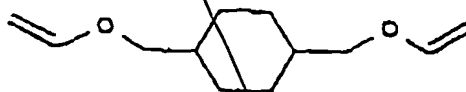
7. The process as claimed in any one of claims 1 to 6, characterized in that the reactive diluent(s) C is (are) chosen:

- 10 → from the nonorganosilicon organic compounds (C_1) possessing CFG + optionally SFG reactive groups having the following formulae:

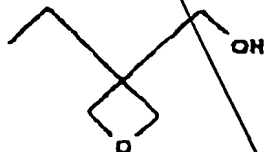
(C_1)



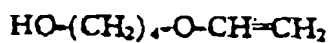
(C_1')



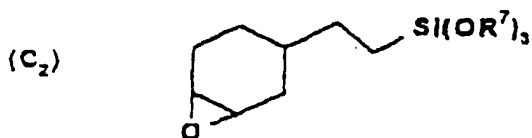
(C_1'')



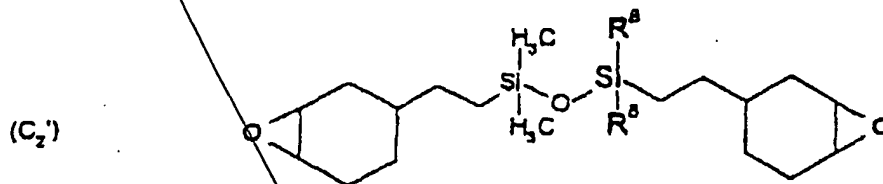
(C_1''')



→ and/or from the organosilicon compounds
(C₂) possessing CFG + optionally SFG reactive groups
having the following formulae:



with R⁷ = C₁-C₁₀ alkyl,



with R⁸ independently representing a C₁-C₁₀ alkyl.

8. The process as claimed in any one of
claims 1 to 7, characterized in that the diluent (C)
exhibits a boiling point B.p. $\geq 100^\circ\text{C}$ at standard
atmospheric pressure and a viscosity at 25°C
 $\eta \leq 100 \text{ mPa.s.}$

9. The process as claimed in any one of
claims 1 to 8, characterized in that, prior to stage 1,
the support to be coated is covered using an adhesion
primer of the type of those comprising at least one
compound chosen from the group consisting of:

- alkoxyated silanes carrying at least one
ethylenic unsaturation and/or at least one epoxide

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functional group,

- (meth)acrylates,
- metal chelates and/or alkoxides,
- crosslinkable silicone compositions and
- 5 compositions which are precursors of silicone elastomers.

Expt A₁

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